

A toy model for molecular condensates in Bose gases

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The occurrence of a molecular Bose-Einstein condensate is studied for an atomic system near a zero energy resonance of the binary scattering process, with a large and positive scattering length. The interaction potential is modeled by a pseudo-potential having one bound state. Using a variational Gaussian ansatz for the N -body density operator, we discuss the thermodynamic properties at low temperature and the relative stability of the system towards the formation of an atomic Bose-Einstein condensate. We also derive an approximate Gross-Pitaevskii equation for the molecular condensate leading to the prediction of a Bogoliubov spectrum.

The atomic Bose-Einstein condensation has been extensively studied during past years both theoretically and experimentally [1,2]. In this Letter, we consider the different case of a molecular Bose-Einstein condensate. The realization of such a situation is a challenge in the field of low temperature physics. Already cold gases of molecules have been produced [3–5]. No evidence for a molecular condensate has been obtained yet, although the stimulated Raman technique used in [5], forming molecules directly from an atomic condensate, is promising.

Another scenario is possible for the formation of the molecular condensate. Consider the case of a so-called *zero-energy* resonance in the two-body scattering process, where the **positive** scattering length $a > 0$ is much larger than the effective range r_e of the interaction potential [6]. In this case the two-body potential supports a s -wave bound state ϕ_0 with a spatial extension $\simeq a$ much larger than the other s -wave bound states and with a much smaller binding energy $E_0 = -\hbar^2/(ma^2)$. One then would rely simply on three-body collisions between atoms of a trapped atomic condensate to produce molecules in the state ϕ_0 . As shown in [7,8] the rate of formation of molecules scales as a^4 in the limit of large a and mainly leads to formation of molecules in the highest s -wave two-body channel [8] that is in the state ϕ_0 . From energy conservation one finds that the molecules produced in ϕ_0 have a kinetic energy $-E_0/3$ when the initial atomic wavevectors \vec{k} are such that $ka \ll 1$. The requirement that the molecules formed in state ϕ_0 remain in the trap imposes a depth of the trapping potential larger than $-E_0$. For a modest trap depth of 10 μ K achievable in an optical trap [9] and for the mass of Rubidium one finds that a has to be larger than 445 Bohr radii. Such high

values of a may be obtained using a Feshbach resonance induced by a magnetic field [10,11].

In this Letter we assume that a condensate of molecules in the diatomic bound state ϕ_0 has been formed. We describe the molecular condensate at the atomic level: we take as a starting point a model Hamiltonian for interacting atoms and we use a Gaussian variational ansatz for the N -body density operator including only the effect of binary interactions between atoms. In the low density regime ($na^3 \ll 1$ where n is the density of atoms) we determine (i) the properties of the molecular condensate at thermal equilibrium and (ii) the response of the molecular condensate to a small perturbation of the trapping potential. Our results for both cases correspond formally to the known properties of a weakly interacting Bose-Einstein condensate of particles of mass $2m$ having a coupling constant $6g$, where m is the atomic mass and $g = 4\pi\hbar^2 a/m$ is the atomic coupling constant. At higher density ($na^3 > \pi/192$) we find that an atomic condensate forms. To model the binary atomic interaction potential we use the pseudo-potential V defined by the following action on a two-body atomic wavefunction ψ :

$$\langle \vec{r}_1, \vec{r}_2 | V | \psi \rangle = g \delta(\vec{r}) \partial_r \left[r \psi(\vec{R} - \vec{r}/2, \vec{R} + \vec{r}/2) \right] \quad , \quad (1)$$

where we have introduced the coordinates of the center of mass and of the relative motion:

$$\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}, \quad \vec{r} = \vec{r}_1 - \vec{r}_2 \quad \text{and} \quad r = \|\vec{r}\| \quad . \quad (2)$$

This model potential discussed in [12] has been used to extend the BCS theory to inhomogeneous atomic systems [13]. As we now see, it has the ability to capture the essential feature of a general binary scattering problem near a zero-energy resonance. Consider indeed the relative motion of two atoms described by the hamiltonian

$$\mathcal{H}_r = -\frac{\hbar^2}{m} \Delta_{\vec{r}} + V \quad . \quad (3)$$

Contrary to the case of the usual contact interaction, the scattering of two atoms interacting with the potential (1) is a well defined problem. The scattering amplitude for a relative wavevector \vec{k} is given by $-a/(1 + ika)$ reproducing the known universal Lorentzian shape of the scattering cross section near a zero energy resonance [6]. In addition to the usual scattering states, the pseudo-potential for $a > 0$ leads to the asymptotic form of the s -wave bound state of energy E_0 :

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$$\phi_0(\vec{r}) = \frac{1}{r (2\pi a)^{1/2}} \exp\left(-\frac{r}{a}\right) \quad . \quad (4)$$

This property of the pseudo-potential reproduces the universal behaviour for a general interaction potential close to a zero-energy resonance, already mentioned in the introduction. It plays an essential role in our approach as it allows the formation of pairs of atoms, that is binary molecules, while keeping the mathematical simplicity of a zero range model potential ($r_e = 0$).

The goal of this paper is to study the properties of a molecular condensate, in a symmetry breaking approach, this corresponds to $\langle \hat{\Psi} \rangle = 0$ and $\langle \hat{\Psi} \hat{\Psi} \rangle \neq 0$, where $\hat{\Psi}$ is the atomic field operator. However it is dangerous to exclude *a priori* the coexistence of an atomic and a molecular condensate. We therefore use the more general symmetry breaking prescription by splitting the field operator in a classical part and a quantum fluctuation part: $\hat{\Psi} = \Phi + \hat{\phi}$, with $\langle \hat{\phi} \rangle = 0$. We choose a Gaussian ansatz for the many-body density matrix $D = Z^{-1} \exp -\beta K$ with

$$K = \int d^3 r_1 d^3 r_2 \hat{\phi}^\dagger(\vec{r}_1) h(\vec{r}_1, \vec{r}_2) \hat{\phi}(\vec{r}_2) + \frac{1}{2} \int d^3 r_1 d^3 r_2 [\hat{\phi}(\vec{r}_1) \Delta(\vec{r}_1, \vec{r}_2) \hat{\phi}(\vec{r}_2) + \text{h.c.}] \quad .$$

There are three variational fields in this theory: h, Δ and Φ . At thermal equilibrium, the grand potential $E - \mu N - TS$ is minimum so that the functions $h(\vec{r}_1, \vec{r}_2)$ and $\Delta(\vec{r}_1, \vec{r}_2)$ may be expressed in terms of the one-body density matrix $\bar{\rho}(\vec{r}_1, \vec{r}_2) = \langle \hat{\phi}^\dagger(\vec{r}_2) \hat{\phi}(\vec{r}_1) \rangle$ and of the pairing function $\bar{\kappa}(\vec{r}_1, \vec{r}_2) = \langle \hat{\phi}(\vec{r}_1) \hat{\phi}(\vec{r}_2) \rangle$, while $\Phi(\vec{r})$ verifies a partial differential equation [14]

$$h(\vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2m} (\vec{\nabla}^2 \delta)(\vec{r}) + (2gn(\vec{R}) - \mu) \delta(\vec{r}) \quad (5)$$

$$\Delta(\vec{r}_1, \vec{r}_2) = g \delta(\vec{r}) [\bar{\kappa}_{\text{reg}}(\vec{R}) + \Phi^2(\vec{R})] \quad (6)$$

$$-\frac{\hbar^2}{2m} \Delta \Phi + [g(2n - |\Phi|^2) - \mu] \Phi + g \bar{\kappa}_{\text{reg}} \Phi^* = 0 \quad (7)$$

In these equations, we have introduced the atomic density at a point \vec{R}

$$n(\vec{R}) = |\Phi|^2(\vec{R}) + \bar{\rho}(\vec{R}, \vec{R}) \quad , \quad (8)$$

and the regular part of the pairing function

$$\bar{\kappa}_{\text{reg}}(\vec{R}) = \lim_{\vec{r} \rightarrow 0} \partial_r \left[r \bar{\kappa}(\vec{R} - \vec{r}/2, \vec{R} + \vec{r}/2) \right] \quad . \quad (9)$$

We assume here that the atoms are in a cubic box of size L with periodic boundary conditions [15], so that $\Phi, n, \kappa_{\text{reg}}$ do not depend on position. We expand the field operator on plane waves using a Bogoliubov transform:

$$\hat{\phi}(\vec{r}) = \frac{1}{L^{3/2}} \sum_{\vec{k}} \hat{b}_{\vec{k}} u_k \exp(i\vec{k} \cdot \vec{r}) + \hat{b}_{\vec{k}}^\dagger v_k^* \exp(-i\vec{k} \cdot \vec{r}). \quad (10)$$

The commutation relations of the bosonic annihilation operators $\hat{b}_{\vec{k}}$'s lead to the normalization of the modes amplitudes $|u_k|^2 - |v_k|^2 = 1$. We search the (u_k, v_k) 's so that K is a sum of decoupled harmonic oscillators:

$$K = K_0 + \sum_{\vec{k}} \hbar \omega_k \hat{b}_{\vec{k}}^\dagger \hat{b}_{\vec{k}} \quad . \quad (11)$$

From the equilibrium conditions (5,6), we find that each (u_k, v_k) is the eigenvector of the system:

$$\begin{aligned} h_k u_k + g(\Phi^2 + \bar{\kappa}_{\text{reg}}) v_k &= \hbar \omega_k u_k \\ h_k v_k + g(\Phi^2 + \bar{\kappa}_{\text{reg}}) u_k &= -\hbar \omega_k v_k \end{aligned} \quad (12)$$

with the notation $h_k = \frac{\hbar^2 k^2}{2m} + 2gn - \mu$. A simple algebra gives the expressions for the eigenvectors and the spectrum $\{\hbar \omega_k\}$ [16]:

$$v_k^2 = \frac{1}{2} \left[\frac{h_k}{\hbar \omega_k} - 1 \right] \quad (13)$$

$$\hbar \omega_k = [h_k^2 - g^2(\Phi^2 + \bar{\kappa}_{\text{reg}})^2]^{1/2} \quad (14)$$

The pairing function is given by

$$\bar{\kappa}(\vec{r}_1, \vec{r}_2) = -\frac{g(\bar{\kappa}_{\text{reg}} + \Phi^2)}{2L^3} \sum_{\vec{k}} \frac{1 + 2f_k}{\hbar \omega_k} \exp(i\vec{k} \cdot \vec{r}) \quad , \quad (15)$$

and the one-body density matrix

$$\bar{\rho}(\vec{r}_1, \vec{r}_2) = \frac{1}{L^3} \sum_{\vec{k}} [(2f_k + 1) v_k^2 + f_k] \exp(i\vec{k} \cdot \vec{r}) \quad . \quad (16)$$

In Eqs.(15,16), f_k is the Bose occupation factor $f_k = [\exp(\beta \hbar \omega_k) - 1]^{-1}$.

All the equilibrium properties may be expressed in terms of (n, T) . For this purpose, we have to determine the three unknown parameters $(\mu, \Phi, \bar{\kappa}_{\text{reg}})$. In the presence of an atomic condensate, Φ does not vanish and a first relation is given by Eq.(7)

$$\mu = g[2n + \bar{\kappa}_{\text{reg}} - \Phi^2] \quad . \quad (17)$$

A second one is obtained from Eq.(8), by setting $\vec{r} = 0$ in Eq.(16)

$$n = \Phi^2 + \frac{1}{L^3} \sum_{\vec{k}} [(2f_k + 1) v_k^2 + f_k] \quad . \quad (18)$$

The third equation is obtained by extracting the regular part of Eq.(15) as in [13]; this leads to

$$\bar{\kappa}_{\text{reg}} = \frac{g(\Phi^2 + \bar{\kappa}_{\text{reg}})}{L^3} \sum_{\vec{k}} \left[\frac{m}{\hbar^2 k^2} - \frac{1 + 2f_k}{2\hbar \omega_k} \right] \quad . \quad (19)$$

In what follows, we consider the thermodynamical limit so that the sums over \vec{k} are replaced by integrals, we also restrict to the case of a vanishing temperature $T = 0$, so that the Bose occupation factors f_k is zero.

First, we note that the stability of the ground state imposes real values for the spectrum $\{\hbar\omega_k\}$, this implies $\bar{\kappa}_{\text{reg}} < 0$ and from Eq.(19), we find $|\bar{\kappa}_{\text{reg}}| > |\Phi|^2$. In particular for a vanishing number of atoms in the condensate $\Phi = 0$, we get from Eqs.(17,18,19):

$$\bar{\kappa}_{\text{reg}}^c = -\frac{\pi}{64a^3} \quad , \quad n^c = \frac{\pi}{192a^3} \quad . \quad (20)$$

This value of the density determines the threshold of coexistence of an atomic condensate ($\Phi \neq 0$) with a molecular one. For $n > n^c$, the model predicts the coexistence, a result already obtained in a slightly different approach in [17]. In this high density regime, our modelization is questionable and we do not pursue the study in this range anymore.

For $n < n^c$, there is no atomic condensate: Φ is identically zero so that Eq.(17) does not hold in this regime and equilibrium properties are deduced from Eqs.(18,19) only. We now wish to check that the low density regime corresponds indeed to a molecular condensate. For this purpose, we suppose that the chemical potential tends to a finite negative value, hence $|\mu| \gg gn, g|\bar{\kappa}_{\text{reg}}|$ and $\hbar\omega_k \simeq \hbar^2 k^2 / (2m) - \mu$. From Eq.(19) we find the lowest order approximation

$$\mu \simeq \frac{E_0}{2} \quad , \quad (21)$$

which is finite indeed, and negative. This result is enlightening: E_0 is just the binding energy of a pair of atoms in the bound state Eq.(4) so that the value Eq.(21) of the chemical potential corresponds to that of an ideal gas of molecules. Since we are at zero temperature this gas of pairs is actually a molecular Bose-Einstein condensate.

This interpretation is confirmed by the lowest order approximation to the pairing function κ in the low density limit. One first calculates $\bar{\kappa}_{\text{reg}}$ from Eq.(18) using the lowest order approximation $v_k \simeq g\bar{\kappa}_{\text{reg}}(E_0 - \hbar^2 k^2 / m)^{-1}$ [18]:

$$\bar{\kappa}_{\text{reg}} \simeq -\frac{1}{a^3} \left(\frac{na^3}{2\pi} \right)^{1/2} \quad , \quad (22)$$

then we calculate the integral over \vec{k} in Eq.(15) and in Eq.(16) to obtain the lowest order contributions to the pairing function and to the one-body density matrix:

$$\bar{\kappa}(\vec{r}_1, \vec{r}_2) \simeq \sqrt{n} \phi_0(r) \quad , \quad \rho(\vec{r}_1, \vec{r}_2) \simeq n \exp\left(-\frac{r}{a}\right) \quad . \quad (23)$$

This expression of $\bar{\kappa}(\vec{r}_1, \vec{r}_2)$ clearly shows that the pairing function describe the spatial structure of two atoms

linked in the molecular bound state ϕ_0 . Similar results have been obtained in [17] for a different model potential.

For a small but finite gaseous parameter na^3 the molecular condensate is not an ideal gas but rather a weakly interacting Bose gas, with an effective coupling constant g_{mol} between the molecules. We derive this coupling constant by calculating the first correction to the expression Eq.(21) for the chemical potential. We expand the expression Eq.(14) to first order in na^3 and substitute the result in Eq.(19). This leads to

$$\mu = \frac{E_0}{2} (1 - 12\pi na^3 + \dots) \quad . \quad (24)$$

On the other hand the molecular chemical potential μ_{mol} , equal to twice the atomic chemical potential μ , is given in the usual mean-field approach for condensates by

$$\mu_{\text{mol}} = E_0 + g_{\text{mol}} n_{\text{mol}} \quad , \quad (25)$$

where $n_{\text{mol}} = n/2$ is the density of molecules. We therefore deduce for the coupling constant between molecules [19]:

$$g_{\text{mol}} = 6g \quad . \quad (26)$$

As g_{mol} is positive the molecular condensate is stable with respect to a spatial collapse.

The value of the molecular coupling constant g_{mol} can also be obtained from the response of the gas to a time dependent perturbation. It is important to check that the corresponding value coincides with the static prediction Eq.(26). Imagine that one perturbs the system from thermodynamical equilibrium by applying an external potential on the atoms for a finite time interval $[0, \tau]$. We describe the evolution of the gas by a time dependent Gaussian ansatz for the many-body density operator [14]. In that case, as in [13], we deduce from the Heisenberg equation for the field operator and from Wick's theorem the time evolution of the pairing function, written here for convenience for $t > \tau$:

$$\begin{aligned} [-i\hbar\partial_t - \frac{\hbar^2}{4m}\Delta_{\vec{R}} + 2(gn(\vec{r}_1) + gn(\vec{r}_2) - \mu) + \mathcal{H}_r] \bar{\kappa}(\vec{r}_1, \vec{r}_2) \\ = -g\bar{\kappa}_{\text{reg}}(\vec{r}_1)\rho^*(\vec{r}_1, \vec{r}_2) - g\bar{\kappa}_{\text{reg}}(\vec{r}_2)\rho(\vec{r}_1, \vec{r}_2) \quad . \quad (27) \end{aligned}$$

We assume that the applied perturbation varies very slowly spatially at the scale of the scattering length a . Thus the pairing function has negligible components on the scattering states and can be assumed to have the same r dependence as ϕ_0 . We therefore take the Local Density Approximation:

$$\bar{\kappa}(\vec{r}_1, \vec{r}_2) = [n(\vec{R}, t)]^{1/2} \phi_0(r) \exp[iS(\vec{R}, t)] \quad . \quad (28)$$

We close equation (27) with the Local Density Approximation for the one-body density matrix:

$$\rho(\vec{r}_1, \vec{r}_2) = n(\vec{R}, t) \exp\left(-\frac{r}{a}\right) . \quad (29)$$

A simple projection of Eq.(27) on the bound state (4) leads to the Gross-Pitaevskii equation

$$i\hbar\partial_t\psi_P = \left(-\frac{\hbar^2}{4m}\Delta_{\vec{R}} + 6g|\psi_P|^2 - 2\mu + E_0\right)\psi_P , \quad (30)$$

where we have introduced the macroscopic wave function $\psi_P(\vec{R}, t) = (n/2)^{1/2} \exp(iS)$ describing the molecular condensate. We note that this equation, confirms in a direct way our previous finding on μ at equilibrium (Eq.(24)). From the linear analysis of Eq.(30), we predict a Bogoliubov spectrum for the molecular condensate different from the atomic condensate:

$$\hbar\omega_P(k) = \left(\frac{\hbar^2 k^2}{4m}\right)^{1/2} \left(\frac{\hbar^2 k^2}{4m} + 6gn\right)^{1/2} . \quad (31)$$

Measurement of this spectrum could be used as an experimental evidence for the condensation of pairs.

As a conclusion let us stress three points. First, one word about the temperature. Indeed, the critical temperature at which the condensate of molecules (mass $2m$, density $n/2$) forms is

$$k_B T_c = \frac{\pi\hbar^2}{m} \left[\frac{n}{2\zeta(3/2)} \right]^{2/3} . \quad (32)$$

In the low density regime $k_B T_c \ll |E_0|$, so that condensation of pairs can occur without any thermal dissociation. Second, it would be interesting to test the prediction on the coupling constant ($6g$) by a direct calculation of the scattering of two molecules of the type considered here. Finally, our model does not describe the relative stability of this molecular condensate toward the formation of molecules in deeper bound levels. An evaluation of the creation rate of deep bound states by collision of an atom with one molecule would be a relevant complement to this analysis.

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